US009291605B2

(12) **United States Patent**
Wagner

(10) **Patent No.: US 9,291,605 B2**
(45) **Date of Patent: Mar. 22, 2016**

(54) **VALVE FOR USE IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY HAVING A SPHERICAL SEAT WITH BEVELED OUTER FACES**

(75) Inventor: **Joachim-Richard Wagner**, Waldbronn (DE)

(73) Assignee: **Agilent Technologies, Inc.**, Santa Clara, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 304 days.

(21) Appl. No.: **12/909,869**

(22) Filed: **Oct. 22, 2010**

(65) **Prior Publication Data**

US 2011/0094954 A1 Apr. 28, 2011

(30) **Foreign Application Priority Data**

Oct. 26, 2009 (DE) 10 2009 045 987
Oct. 7, 2010 (DE) 10 2010 042 107

(51) **Int. Cl.**

G01N 30/36	(2006.01)
F16K 1/42	(2006.01)
F16K 25/00	(2006.01)
G01N 30/32	(2006.01)

(52) **U.S. Cl.**

CPC ***G01N 30/36*** (2013.01); ***F16K 1/42*** (2013.01); ***F16K 25/005*** (2013.01); *G01N 2030/328* (2013.01)

(58) **Field of Classification Search**

CPC F16K 1/42; F16K 25/005; G01N 30/36; G01N 2030/328
USPC 210/656, 198.2; 251/318
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,456,440	A	6/1984	Korner et al.	
4,883,409	A	11/1989	Strohmeier et al.	
4,945,945	A *	8/1990	Schmid	137/512
4,974,628	A	12/1990	Tepermeister et al.	
2009/0076631	A1	3/2009	Witt et al.	
2009/0104083	A1 *	4/2009	Aso	422/103

FOREIGN PATENT DOCUMENTS

CN	101418868	A	4/2009
DE	3111614	A1	7/1982
DE	202006018959		2/2007
DE	102009001756	A1	7/2009
EP	0309596	A1	4/1989
JP	2000283309	A1	10/2000
JP	2005133850	A	5/2005

(Continued)

OTHER PUBLICATIONS

PTO Translation No. 13-1097 of Japan Patent No. 2005133850.*

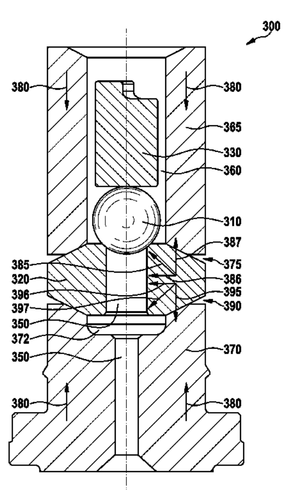
(Continued)

Primary Examiner — Ernest G Therkorn

(57) **ABSTRACT**

A valve for use in high-performance liquid chromatography has a spherical seat and a ball that, when it abuts against the seat, constrains a fluid from flowing through the valve and is capable of moving axially in order to allow the fluid to flow through the valve. The spherical seat has beveled outer faces in order that a force acting on the valve along the axial direction will generate a force acting on the ball. The inclination of the beveled outer face is such that a force acting on the ball counteracts a force exerted on the spherical seat by the ball and essentially compensates it.

12 Claims, 4 Drawing Sheets



(56) **References Cited**

FOREIGN PATENT DOCUMENTS

JP	2005133850 A1	5/2005
JP	2006214539 A1	8/2006

OTHER PUBLICATIONS

PTO Translation No. 13-1096 of Japan Patent No. 2000283309.*
PTO Translation No. 13-1095 of Japan Patent No. 2006214539.*
Office Action mailed Jul. 16, 2014 for Chinese Patent Application No. 201010531385.6.
Office Action mailed Dec. 18, 2013 for Chinese Patent Application No. 201010531385.6.
Office Action mailed Mar. 23, 2015 in German Patent Application No. 102010042107.3 (Unofficial/Non-certified translation provided by foreign agent included).
Machine translation of DE202006018959, Feb. 22, 2007.
Office Action mailed Jan. 22, 2015 in Chinese Patent Application No. 201010531385.6 (Unofficial/non-certified translation provided by foreign agent included).
Office Action mailed Oct. 4, 2015 in Chinese Patent Application No. 201010531385.6 (Unofficial/non-certified translation provided by foreign agent included).

* cited by examiner

Fig. 1

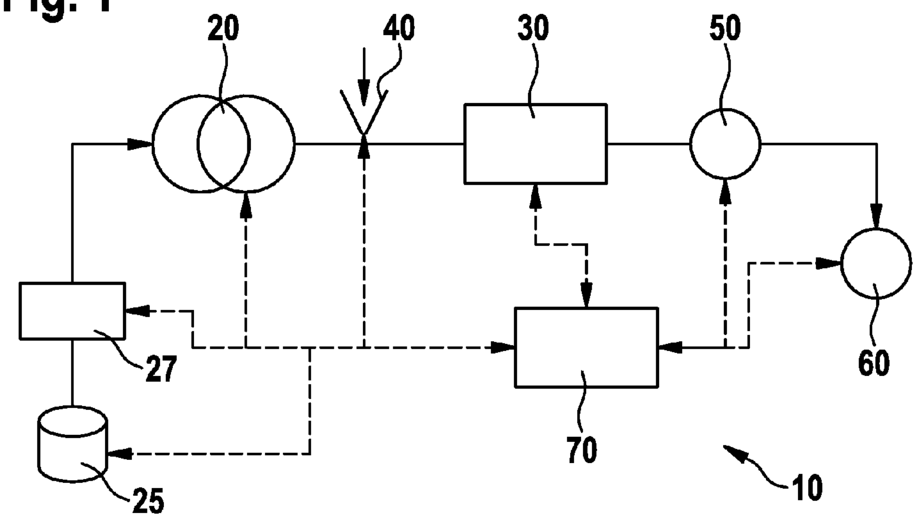


Fig. 2

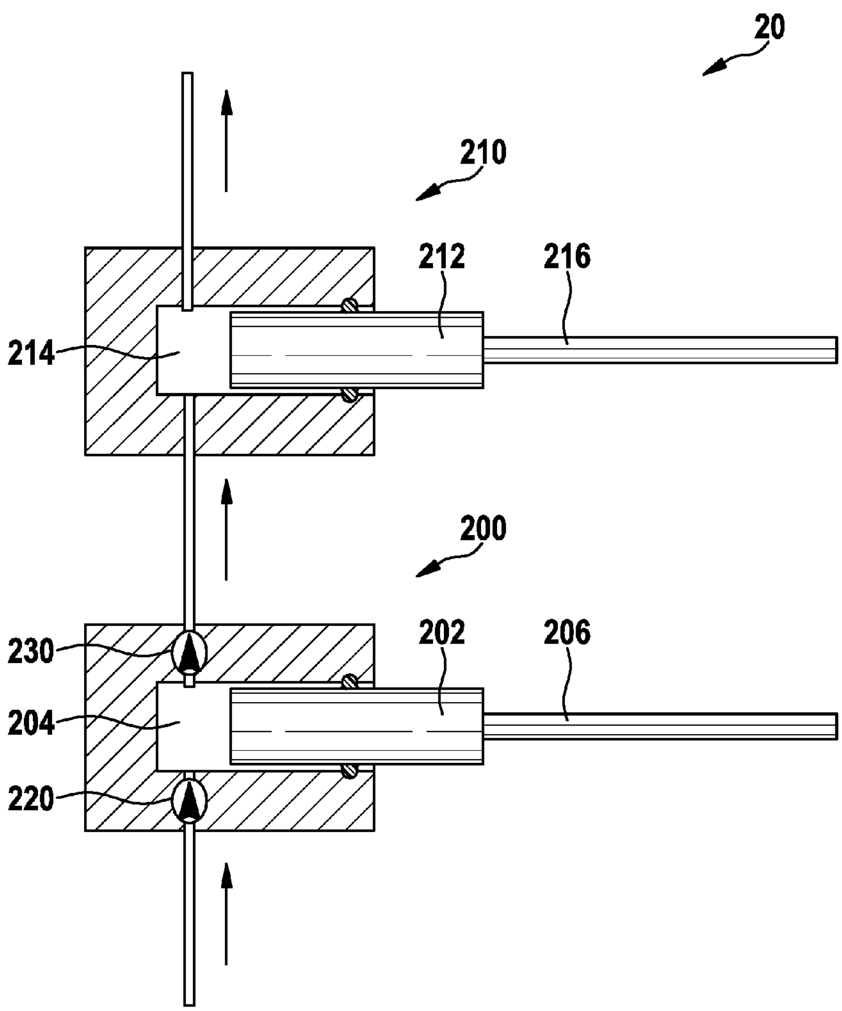


Fig. 3

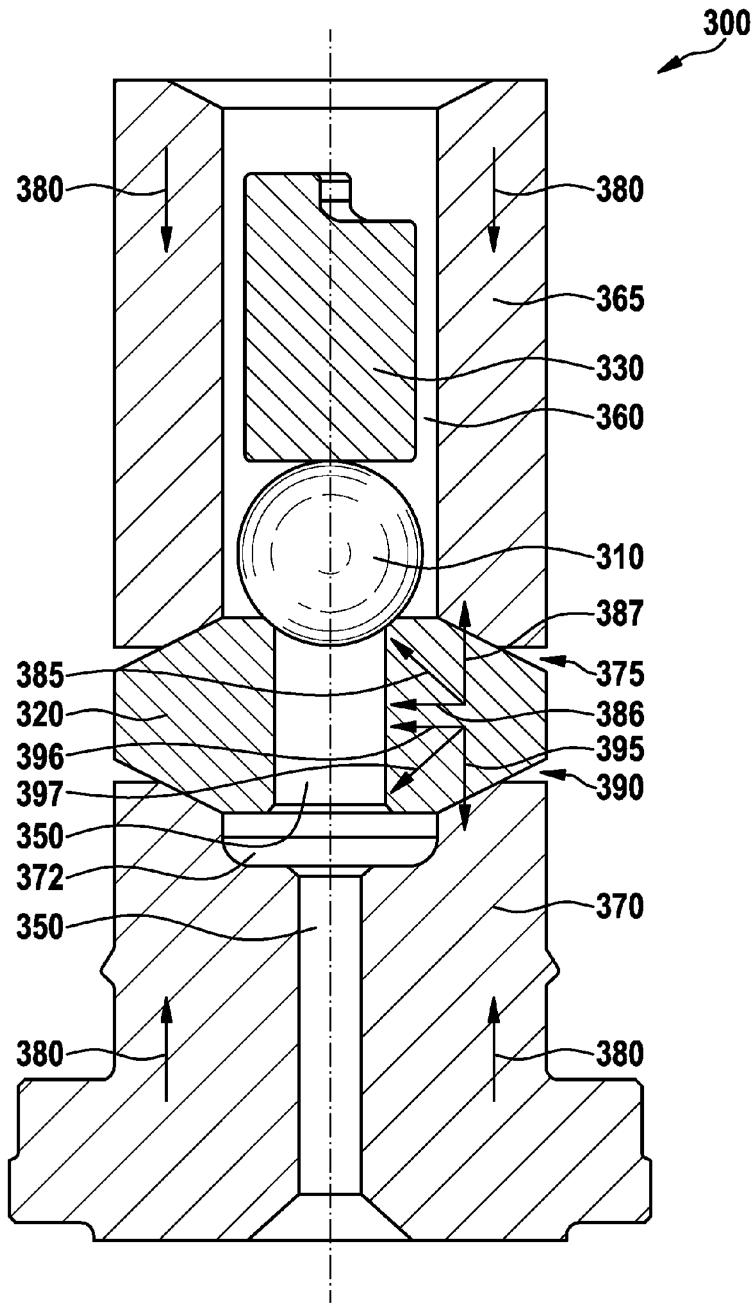
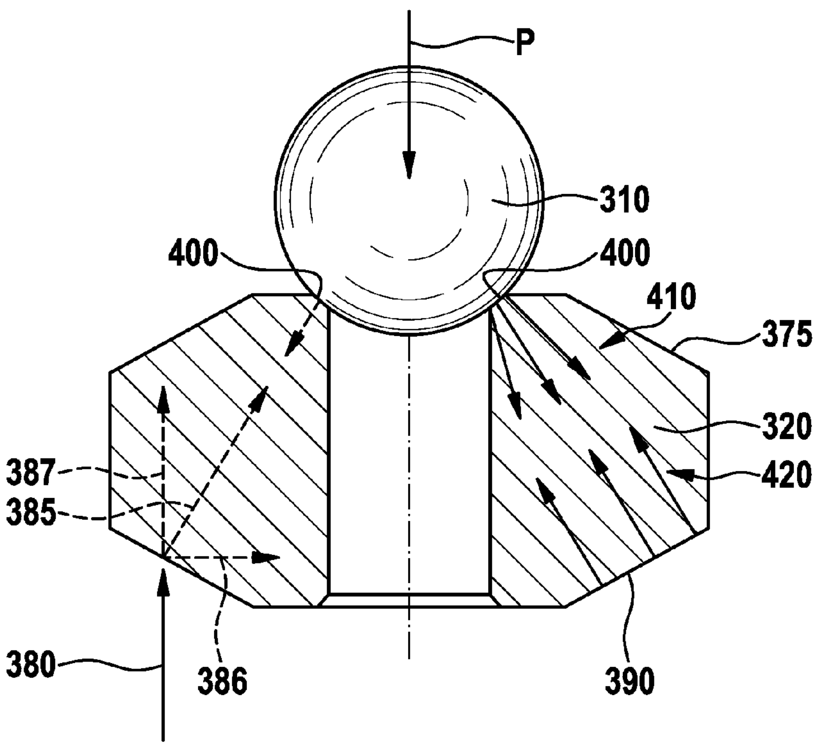

300
380
380
365
330
360
310
387
385
375
320
386
396
395
397
390
350
372
350
370
380
380

Fig. 4



VALVE FOR USE IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY HAVING A SPHERICAL SEAT WITH BEVELED OUTER FACES

BACKGROUND

The present invention concerns a valve for use in high-performance liquid chromatography having a ball and a stricture that may be closed by the ball such that a fluid will be constrained from flowing through the valve.

In high-performance liquid chromatography (HPLC), a liquid must be propelled at typically very stringently controlled flow rates varying from, e.g., nanoliters/min. to milliliters/min., and high pressures typically falling within the range 20-100 MPa (200-1,000 bar) and beyond, and currently extending up to around 200 MPa (2,000 bar), where the compressibility of the liquid involved becomes evident. Liquid separation in an HPLC system involves forcing a mobile phase that, during operation, comprises a sample liquid containing components that are to be separated, through a stationary phase, such as a chromatographic column, in order to separate the various components of the sample liquid.

A serial arrangement of a pair of pumps for continuously propelling a liquid into an HPLC system is known from EP 0309596 A1. An outlet valve is situated between the primary pump and secondary pump in order to provide both that the primary pump will be unable to propel liquid into the system until the system pressure has been reached and that the secondary pump will pump liquid into the system, but not back into the primary pump.

Valves, such as outlet and/or inlet valves, are typically configured as passive check valves, where a ball is pressed against the spherical seat by the system pressure, i.e., by the pressure dropping across the ball, in order to constrain a fluid from flowing through the valve, where the ball is capable of moving in the axial direction and being lifted off the spherical seat in order to allow the fluid to flow through the valve. Active valves may also be similarly configured and employed as check valves.

Check valves are sufficiently well known from the state of the art and described in, among others, U.S. Pat. No. 4,945,945 A, U.S. Pat. No. 4,974,628 A, US 2009/104083 A1, DE 202006018959 U1, JP 2000283309 A, JP 2005133850 A, or JP 2006214539 A. A valve seat for high-pressure pumps, in particular, a valve seat for handling pressures exceeding 2,000 bar, is known from DE 3111614 A1.

DISCLOSURE

The problem addressed by the present invention is making available a valve for use in high-performance liquid chromatography that is particularly suitable for use at very high pressures. That problem is solved by a valve having those characteristics stated in the independent claim. Further beneficial embodiments thereof are stated in the dependent claims.

Under an embodiment of the invention, a valve for use in high-performance liquid chromatography has a spherical seat and a ball that, when it abuts against the spherical seat, constrains a fluid from flowing through the valve and is capable of moving axially in order to allow fluid to flow through the valve. The spherical seat has beveled outer faces in order that a force acting on the valve along the axial direction will generate a force acting on the ball. The inclinations of its beveled outer faces are such that the force acting on the ball counteracts a force exerted on the spherical seat by the ball and essentially compensates it, which allows accommodating a radial force exerted on the spherical seat by the ball and combats damage to, or destruction of, the spherical seat.

Under an embodiment, the force exerted on the ball has a radial component.

The force exerted on a sealing edge of the spherical seat by the ball may have a first planar force field and the force acting on the ball may have a second planar force field and is opposingly superimposed on the first force field and essentially compensates it.

The force exerted on the ball may exceed a force exerted on the spherical seat by the ball.

Under an embodiment, a restoring force that presses the ball against the spherical seat acts on the ball in order to constrain the fluid from flowing through the valve. That restoring force may be generated by a drop in system pressure across the ball, as well as by a spring, a weight, the ball's weight, an elastomer, etc.

The spherical seat and/or the ball may, preferably, consist of a ceramic, ruby, or sapphire material.

Under an embodiment, a first, beveled, outer face of the spherical seat abuts against a first housing component of the valve. A second, beveled, outer face of the spherical seat may, preferably, abut against a second housing component of the valve.

Under an embodiment, the normals to the surfaces of the beveled outer faces of the spherical seat are inclined relative to a direction, along which the fluid flows. Their inclinations may fall within the range 20°-70°, preferably within the range 30°-60°, and, more preferably, are about 45°.

A high-performance liquid-chromatography system according to the present invention has a pump for propelling a mobile phase, a stationary phase for separating components of a sample liquid brought into the mobile phase, and a valve, as stated above, that is situated in a flow path of the mobile phase. The high-performance liquid-chromatography system may also have a sample injector for bringing the sample liquid into the mobile phase, a detector for detecting separated components of the sample liquid, and/or a fractioning device for outputting the separated components of the sample liquid.

Embodiments of the present invention may be based on many of the known HPLC systems, such as the Agilent Infinity 1290, 1260, 1220, and 1200 series of the applicant, Agilent Technologies, Inc. Cf. www.agilent.com.

A pure solvent, or a mixture of various solvents, may be employed as the mobile phase, or eluent. The mobile phase may be chosen such that the retention times of the components of interest and/or the quantities of the mobile phase needed for pursuing chromatography will be minimized. The mobile phase may also be chosen such that certain components will be efficiently separated. The mobile phase may be an organic solvent, such as methanol or acetonitrile, which frequently will be diluted with water. Water and an organic solvent, or another solvent commonly employed in HPLC, are frequently employed when running in gradient mode, under which their mixing ratio is varied over time.

DESCRIPTION OF THE DRAWINGS

The invention will be explained in greater detail below by way of references to the drawings, where the same reference symbols refer to the same, or functionally equivalent or similar, characteristics.

FIG. **1** depicts a liquid-separation system **10** corresponding to embodiments of the present invention, as employed in, e.g., HPLC.

FIG. **2** depicts an embodiment of the pump **20**.

FIG. **3** depicts an embodiment of a valve **300** according to the invention.

FIG. **4** schematically depicts the forces acting within the spherical seat **320**.

In particular, FIG. **1** depicts a generalized representation of a liquid-separation system **10**. A pump **20** receives a mobile phase from a solvent supply **25**, typically via a degasser **27** that degasses the mobile phase and thereby reduces the quantities of dissolved gases present in the mobile phase. The pump **20** propels the mobile phase through a separation device **30**, such as a chromatographic column, having a stationary phase. A sample device, or sample injector **40**, may be provided between the pump **20** and the separation device **30** in order to allow bringing a sample fluid into the mobile phase. The stationary phase of the separation device **30** has been adapted to separating components of the sample fluid. A detector **50** detects the separated components of the sample fluid, and a fractioning device **60** may be provided for outputting the separated components.

The mobile phase may consist of a single solvent or a mixture of various solvents. Their admixing may be performed at a low pressure and ahead of the pump **20** in order that the pump **20** will propel the solvent mixture as the mobile phase. Alternatively, the pump may consist of discrete pumping units, where every pumping unit propels a single solvent, or solvent mixture, in order that the admixing of the mobile phase, as seen by the separation device **30**, occurs under high pressure, and following the pump **20**. The composition (mixing ratio) of the mobile phase may be either held constant over time (isocratic mode) or varied over time under what is termed "gradient mode."

A data-processing unit **70**, which may be either a conventional PC or a workstation, may be interfaced to one or more devices on the liquid-separation system **10**, as indicated by the arrows and dashed lines, in order to allow it to acquire data and/or operate the system or control individual components thereof.

FIG. **2** depicts an embodiment of the pump **20**, as known from the aforementioned EP 0309596 A1. The pump **20** consists of a serial arrangement of a primary pump **200** and a secondary pump **210** in order to provide for continuous propulsion of liquid through the HPLC system **10**. The primary pump **200** has a displacement piston **202** that may be moved back and forth in a cylinder **204** by a drive **206**, schematically depicted in the form of a connecting rod, in order to induct and expel liquid. The secondary pump **210** also has a displacement piston **212** that may be moved back and forth in a cylinder **214** by a drive **216**, schematically depicted in the form of a connection rod, in order to induct and expel liquid.

In the case of this embodiment, an inlet valve **220** is situated at the inlet to the pump **200**, and an outlet valve **230** is situated at its outlet. These valves may be, and preferably are, configured in the form of passive check valves. The inlet valve **220** allows induction of liquid by the primary pump's piston **202**, but prevents inducted liquid present in the cylinder **204** from being expelled through the valve **220** when it is displaced by the piston. The outlet valve **230** remains closed during an induction stroke by the primary pump's piston **202** and opens when the inducted liquid present in the cylinder **204** is expelled, once the system pressure, i.e., the pressure downstream from the valve **230**, or, in other words, the pressure under which the liquid is propelled through the column **30**, has been reached. Correspondingly, the outlet valve **230** between the primary pump **200** and the secondary pump **210** provides both that the primary pump **200** is unable to propel liquid into the system until the system pressure has been reached and that the secondary pump **210** propels liquid into the system, but not back into the primary pump **200**. The outlet valve **230** may also be configured in the form of a redundant, dual-ball valve in order to improve system reliability.

FIG. **3** depicts a valve **300** according to an embodiment of the invention that might, for example, be situated at any location where the valves **220** and **230** shown in FIG. **2** might be situated. A ball **310** abuts against a spherical seat **320**, where a restoring force **330** presses the ball **310** against the spherical seat **320** in order that the ball **310** will block a flow channel **350**. The ball **310** will not open the flow channel **350** and allow liquid to flow past it and into the adjacent flow channel **360** until the pressure exerted on it by the liquid exceeds the pressure exerted on it by the restoring force **330**.

The restoring force **330** schematically depicted in FIG. **3** represents both a drop in system pressure across the ball **310** and another force, such as a force exerted by a spring, as depicted in the aforementioned DE 202006018959 U1, a weight, the ball's weight, an elastomer, etc. A pushrod (not shown) that protrudes through the spherical seat **320** and lifts the ball **310**, and, for example, might be actuated by a solenoid, may also be employed for opening the valve **300**. Combinations of the aforementioned means might also be utilized for generating the restoring force **330**.

The spherical seat **320** is surrounded by a first housing component **365** and a second housing component **370** and held in place by them. In the case of the example shown in FIG. **3**, the ball **310** is encircled by the first housing component **365** and the latter encloses the flow channel **360**, while the second housing component **370** encloses the flow channel **350**. FIG. **3** also depicts an optional cavity **372** that can benefit flushability.

A first outer surface **390** of the spherical seat **320** abutting against the second housing component **370** is beveled in order that a force **380**, portrayed in FIG. **3** in the form of upward and downward compressive forces, acting on the valve along the axial direction generates a force **385** acting on the ball **310** that has a radial component **386** and an axial component **387**. The effects of the force **385** acting on the ball **310** will be described in detail below. In the case of the example shown in FIG. **3**, the spherical seat **320** also has a second outer face **375** abutting against the first housing component **365** that has a bevel whose inclination is inverted with respect to that of the bevel on the first outer face **390**.

The sides of the housing components **365** and **370** abutting against the outer faces **375** and **390** are, preferably, also beveled in order to provide for good contacts between their respective abutting surfaces. The degree of sealing action occurring between the spherical seat **320** and the housing components **365** and **370** may be adjusted by configuring their abutting surfaces. For example, sealing action may be increased by reducing the areas of their abutting surfaces, as indicated in FIG. **3**. Coating the housing components **365** and **370** with materials, such as gold, PEEK, elastomers, etc., that benefit that sealing action, or choosing suitable elastic materials, may allow attaining suitably adjusted sealing actions.

The radial force components **386** and **396** counteract the radial forces exerted on the spherical seat **320** resulting from the ball **310** being pressed against the spherical seat **320** that might cause a radial deformation (enlargement) of the spherical seat, and thus decrease both the likelihood of leaks and risks that breakage of the spherical seat **320** might occur under peak loading by those radial forces. A single beveled outer face **390** or **375** will be sufficient to generate those radial force components.

The valve **300** shown in FIG. **3** may also be enclosed by an outer housing (not shown), against which, e.g., the housing components **365** and **370** and/or the spherical seat **320** may abut.

The inclination of the beveled outer face **390** of the spherical seat **320** is determined by the location of the sealing edge of the spherical seat **320** relative to the ball **310** and the direction of the vector representing the resultant of those forces exerted on the spherical seat **320** by the ball **310**, as will be explained in detail in conjunction with FIG. **4**.

FIG. **4** schematically depicts the forces acting within the spherical seat **320**, where the relationships shown in FIG. **4** are referenced to the installed status shown in FIG. **3**. The ball **310** is pressed into the spherical seat **320** by the system pressure, P, schematically represented by an arrow, acting within the mobile phase and abuts against a sealing edge **400**. The sealing edge **400** represents the surface on the spherical seat **320** contacted by the ball **310** and yields a sealing action of the valve **300** whenever the ball **310** is pressed into the spherical seat **320**. The sealing edge **400** is typically a ground-in, spherical surface. Pressing the ball **310** against the sealing edge **400** on the spherical seat **320** generates a planar force field **410**. An oppositely directed force field **420** must be generated in order to prevent deformation of the spherical seat **320** by the force field **410**. That force field **420** is due to the force **385**, whose direction is determined by the inclination of the outer face **390**, relative to the axial direction. The inclination of the outer face **390** should therefore be chosen such that the force fields **410** and **420** will ideally be opposingly superimposed on one another and thus compensate one another.

Due to the clamping action spread over the beveled surface **390**, an oppositely directed force field **420** will be exerted on the ball **310** via the sealing edge **400** if the beveled surface's inclination has been correctly chosen. Suitable spatial configurations of the spherical seat **320**, and, in particular, the outer face **390**, in relation to the second housing component **370** will allow providing that the pair of force fields is essentially symmetrically superimposed on one another and thus yield a uniformly distributed compensation of the acting forces.

The force ratio, i.e., the ratio of the force fields **410** and **420**, is duly chosen such that the clamping of the spherical seat **320** yields a greatly increased force **385** in order that the weaker force exerted on the sealing edge **400** by the ball **310** will be insufficient to cause deformation of the spherical seat **320** along the sealing edge **400**. The dimensional stability of the spherical seat **320** will thus be maintained, even at peak force levels (peak pressure levels).

The designations "beveled" or "bevel" refer to an angling of the outer faces **375** and **390** relative to the axial direction such that the normals to their surfaces are inclined at included angles of less than 90° with respect to the axial-direction vector, represented by the arrow **380**. In the case of the example shown in FIG. **3**, the inclinations of their beveled surfaces are approximately 30°-60°, and preferably 40°. Obviously, their inclinations must be oriented such that the radial force components **386** and **396** are directed inward, i.e., toward the ball **310**, as shown in FIG. **3**. The inclinations of the outer faces **375** and **390** are thus inversely oriented, relative to one another.

In the case of a sample embodiment, the normal(s) to the beveled outer faces **375** and/or **390** of the spherical seat **320** are inclined relative to a flow direction of the fluid, where their inclination angle(s) may fall within the range 20°-70°, preferably within the range 30°-60°, and, more preferably, are about 45°.

The designations "axial" and "radial" refer to the sample embodiment of a cylindrical, essentially rotationally symmetric, valve **300** shown in FIG. **3**. The same applies to other forms of the valve **300**, such as rectangular embodiments, in which case, "axial" would essentially refer to the flow direction, or a direction opposite to the flow direction, and "radial" would refer to directions orthogonal thereto.

The spherical seat **320** and/or ball **310** may consist of a ceramic, ruby, or sapphire material, such as SiC, sintered SiC(SSiC), Al_2O_3, ZrO, or combinations thereof, where, e.g., either the entire spherical seat **320**, or at least that portion thereof against which the ball **310** abuts, may be fabricated from the ceramic material. Under an embodiment, both the ball **310** and spherical seat **320**, i.e., that zone of the stricture on which the ball acts, are typically fabricated from a ceramic material. The spherical seat **320** may also consist of a sapphire material and the ball **310** of a ruby material. Furthermore, the ball may be fabricated from a ruby material, while the spherical seat consists of a ceramic material. Those combinations of materials both allow employing very high pressures and have proven particularly suitable for use in conjunction with employment of a wide variety of solvents. Pressures of 1,000 bar and more may be employed without the spherical seat cracking. The other components of the valve may consist of known materials or combinations thereof, such as SST, PEEK, or PEEK constituents.

The invention claimed is:

1. A valve for use in high-performance chromatography, comprising;

a spherical seating structure having a sealing surface, and

a ball configured for constraining, when it abuts against the sealing surface of the spherical seating structure, a fluid from flowing through the valve and for moving in an axial direction in order to allow the fluid to flow through the valve,

wherein the spherical seating structure has a beveled outer face separate and apart from the sealing surface, the beveled outer face being inclined with respect to the axial direction, cooperating with a housing structure and being configured such that a force acting on the valve along the axial direction generates a force acting on the ball, and

wherein the inclination of the beveled outer face is configured such that the force acting on the ball counteracts a force exerted by the ball on the spherical seating structure and essentially compensates it.

2. The valve according to claim **1**, wherein the force acting on the ball has a component along the radial direction.

3. The valve according to claim **1**, wherein the force exerted by the ball on the sealing surface of the spherical seating structure is a first planar force field, and the force acting on the ball is a second planar force field and opposingly superimposed on the first force field and essentially compensates it.

4. The valve according to claim **1**, wherein a restoring force acting on the ball is configured to press the ball against the sealing surface of the spherical seating structure in order to constrain the fluid from flowing through the valve.

5. The valve according to claim **4**, wherein the restoring force acting on the ball is due to a spring, a weight, the weight of the ball, and/or an elastomer.

6. The valve according to claim **1**, wherein at least one of the spherical seating structure and the ball comprises at least one of a ceramic, ruby, or sapphire material.

7. The valve according to claim **1**, wherein the spherical seating structure includes a second beveled outer face abuts against a second housing component.

8. The valve according to claim **1**, wherein the beveled outer face is inclined with respect to the axial direction by an inclination within a range of 20°-70°.

9. The valve according to claim **8**, wherein the inclination is within a range of 30°-60°.

10. The valve according to claim **8**, wherein the inclination is about 45°.

11. A high-performance liquid-chromatography system having a pump configured for moving a mobile phase, a stationary phase configured for separating components of a sample liquid comprised into the mobile phase, and a valve, according to claim **1** situated in a flow path of the mobile phase.

12. The high-performance liquid-chromatography system according to claim **11**, comprising at least one of: a sample injector configured for injecting the sample liquid into the mobile phase; a detector configured for detecting separated components of the sample liquid; a fractioning device configured for outputting separated components of the sample liquid.

* * * * *